National Institute of Standards and Technology

Certificate of Analysis

Standard Reference Material® 2683b

Sulfur in Coal

This Standard Reference Material (SRM) is intended primarily for use in the evaluation of methods and for the calibration of instruments used to determine sulfur in coal. Each unit of SRM 2683b consists of 50 g of bituminous coal that was ground to pass a 60 mesh (250 μm) sieve, homogenized, and bottled under an argon atmosphere.

The certified value for sulfur, reported in Table 1 as a mass fraction [1] on a dry basis (see Instructions for Use), is based on measurements by isotope dilution thermal ionization mass spectrometry (ID-TIMS) [2]. The uncertainty in the certified value is expressed as an expanded uncertainty, U, and is calculated according to the method in the ISO Guide [3]. The expanded uncertainty is calculated as, $U = ku_c$, where u_c is the combined standard uncertainty and k is a coverage factor. The value of u_c represents, at the level of one standard deviation, the combined effect of uncertainty components associated with material inhomogeneity and ID-TIMS measurement uncertainty. The expanded uncertainty (U) is a 95 % prediction interval [4]. The coverage factor, $k = 2.035$, is the value from the t-distribution corresponding to thirty-three degrees of freedom.

Table 1. Certified Value (Dry Basis)

Sulfur	1.955 % ± 0.041 %

The reference value for ash [5,6], reported in Table 2 as a mass fraction on a dry basis (see Instructions for Use), is based on results from 62 laboratories participating in an interlaboratory study done in cooperation with Canada Centre for Mineral and Energy Technology (CANMET) Service Program for the Evaluation of Codes and Standards (CANSPECS). The uncertainty in Table 2 is given as an expanded uncertainty as described in the ISO Guide. The expanded uncertainty is a 95 % prediction interval and includes components for within-laboratory measurement uncertainty, between-laboratory uncertainty, material inhomogeneity and the uncertainty in the conversion of samples dried in air to a nitrogen basis. The coverage factor for this interval, $k = 2.013$, is the value from the t-distribution corresponding to forty-six degrees of freedom.

Table 2. Reference Value (Dry Basis)

Ash	9.93 % ± 0.08 %

Expiration of Certification: This certification is valid until **31 December 2010** within the measurement uncertainties specified, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see Instructions for Use). However, the certification will be nullified if the SRM is contaminated or modified.

The overall direction and coordination of the technical measurements leading to certification was performed by G.C. Turk of the NIST Analytical Chemistry Division.

The support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Standard Reference Materials Program by B.S. MacDonald.

Gaithersburg, MD 20899
Certificate Issue Date: 27 October 1997

Thomas E. Gills, Chief
Standard Reference Materials Program

Certification analyses by ID-TIMS were performed by W.R. Kelly, T.L. Quinn, and R.D. Vocke of the NIST Analytical Chemistry Division. X-ray fluorescence homogeneity analysis was performed by A.F. Marlow of the NIST Analytical Chemistry Division.

Statistical consultation was provided by W.F. Guthrie of the NIST Statistical Engineering Division.

The coal for this SRM was donated by the Illinois State Geological Survey, Champaign, IL and Electric Fuels Corporation, St. Petersburg, FL.

NOTICE AND WARNINGS TO USERS

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

Instructions for Use: To relate analytical determinations to the certified sulfur value, a minimum sample mass of 150 mg should be used. To relate analytical determinations to the reference ash value, a nominal sample weight of 1 g should be used. In each case the sample should be dried according to the Instructions for Drying. When not in use, the SRM must be stored in an air conditioned or similar cool and dry environment away from sunlight and fumes.

Instructions for Drying: In order for users to directly relate their measurements to the certified and reference values, drying corrections should be measured and applied at the time of the analysis. The correction for sulfur and/or ash analysis is determined by drying separate 1 g samples in a nitrogen atmosphere at 105 °C to a constant weight. During drying at NIST, the weight loss of SRM 2683b samples were observed to stabilize after approximately 50 minutes. The average weight loss measured at NIST for SRM 2683b was 3.86 %, with a standard uncertainty of 0.03 % [2].

At NIST a study was also conducted to quantify the difference between drying in air and nitrogen atmospheres for SRM 2683b. The average weight loss determined at NIST for SRM 2683b dried in air was 3.65 %, with a standard uncertainty of 0.03 %.

PREPARATION, HOMOGENEITY TESTING, AND ANALYSIS

Preparation: SRM 2683b is a 50/50 blend of Illinois State Geological Survey IBC-112 coal, (Herrin, Illinois No. 6 coal) and Electric Fuels Corporation SPC-B Coal, (a blend of various coal seams found in Harlan County, KY). Each coal was crushed to a nominal 8 mesh (4.76 mm) particle size and subsequently pulverized until the entire lot passed a 60 mesh sieve (250 mm). Next, the two coals were combined and mixed into a single lot. The entire lot was then divided by the spinning riffle technique into two portions. One portion was stored in bulk under an argon atmosphere. The other portion was further divided into SRM units by the spinning riffle technique and bottled under an argon atmosphere.

Homogeneity Testing: Thirty bottles from the lot were selected for homogeneity testing. Samples from each bottle were analyzed by x-ray fluorescence for sulfur and by ASTM D 3174 for ash [5]. In each case components of variation attributed to bottle-to-bottle variability were detected. The standard deviation of random bottle-to-bottle differences in sulfur concentration is estimated to be 0.96 % ± 0.27 % relative to the certified sulfur concentration. The standard deviation of random bottle-to-bottle differences in ash content is estimated to be 0.23 % ± 0.17 % relative to the reference value given for ash. Homogeneity estimates for both constituents are 95 % confidence intervals.

Analysis: Sulfur determinations by ID-TIMS and homogeneity testing by x-ray fluorescence were performed by the NIST Analytical Chemistry Division. Analysis of the sulfur data was performed in the NIST Statistical Engineering Division. The reference value and its uncertainty given in Table 2 are based on data obtained from an interlaboratory study done in cooperation with Canada Centre for Mineral and Energy Technology (CANMET)

Service Program for the Evaluation of Codes and Standards (CANSPECS) with statistical analysis being performed by the NIST Statistical Engineering Division. SRM 2683b was included as an unknown coal in the CANSPECS 52 Coal Round Robin study. Dry ash data from the study were corrected for moisture content based on samples dried in either air or nitrogen atmospheres. All ash values were converted to a nitrogen drying basis based on a drying study conducted at NIST.

Supplemental Information: The information values given in Table 3 are from the CANSPECS 52 Coal Round Robin study. These values are not certified and are given as additional information on the matrix.

Table 3. Information Values (Dry Basis)

Chlorine	1125 mg/kg
Pyritic Sulfur	0.71 %
Sulphate Sulfur	0.08 %
Gross Calorific Value	30.62 $MJ*kg^{-1}$ (13163 $Btu*lb^{-1}$)
Volatile Matter	36.31 %

In order to demonstrate user experience with this material by conventional methods for sulfur and ash, summary statistics for total sulfur and ash as reported in the CANSPECS 52 Coal Round Robin, are given in Table 4. The most common methods of analysis performed by the participating laboratories were ASTM D 4239 [7] for total sulfur and ASTM D 3174 [5] for ash. The round robin results were not used in calculating the certified sulfur value for SRM 2683b.

Table 4. Summary Statistics for Total Sulfur and Ash as Reported in the CANSPECS 52 Coal Round Robin (in % Dry Basis)

Analyte	n	Mean	Repeatability as Measured	ASTM Repeatability	Reproducibility as Measured	ASTM Reproducibility
Total Sulfur	76	1.94	0.05	0.11 (D 4239)	0.12	0.17 (D 4239)
Ash	79	9.90	0.14	0.30 (D 3174)	0.23	0.50 (D 3174)

REFERENCES

[1] Taylor, B.N., "Guide for the Use of the International System of Units (SI)," NIST Special Publication 811, 1995 Ed., (April 1995).

[2] Kelly, W.R., Paulsen, P.J., Murphy, K.E., Vocke, R.D., and Chen, L.-T. "Determination of Sulfur in Fossil Fuels by Isotope Dilution Thermal Ionization Mass Spectrometry," Anal. Chem., **66**, p. 2505, (1994).

[3] *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed. ISO, Geneva, Switzerland, (1993): see also Taylor, B.N. and Kuyatt, C.E., "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," NIST Technical Note 1297, U.S. Government Printing Office, Washington DC, (1994).

[4] Hahn, G.J., and Meeker, W.Q., "Statistical Intervals: A Guide for Practitioners," John Wiley & Sons, Inc., New York, (1991).

[5] ASTM D 3174-93, "Test Method for Ash in the Analysis Sample of Coal and Coke from Coal," **Vol. 05.05** ASTM Book of Standards, West Conshohocken, PA.

[6] ASTM D 5142-90, "Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures," **Vol. 05.05** ASTM Book of Standards, West Conshohocken, PA.

[7] ASTM D 4239-94, "Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Combustion Methods, **Vol. 05.05** ASTM Book of Standards West Conshohocken, PA.

It is the responsibility of users of this SRM to assure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: Phone: (301) 975-6776 (select Certificates), Fax: (301) 926-4751, e-mail: srminfo@nist.gov, or WWW: http://ts.nist.gov/srm.